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(54) **Method for manufacturing a fabric reinforced composite article having ballisticresistance**

(57) Aliphatic polyamide filament yarn fabrics and aromatic polyamide filament yarn fabrics are respectively dipped into a solution of resin, dried, made into prepregs, cut into proper size, stacked with aliphatic polyamide prepregs as the outer layers and aromatic polyamide prepregs as the inner layers to the extent of a predetermined thickness, and heated and pressurized, wherein the aliphatic polyamide filament yarn fabrics are heat-treated, and then the aliphatic polyamide filament yarn fabrics and aromatic polyamide filament yarn fabrics are pre-heated prior to dipping into a solution of the resin. The article may be a bulletproof helmet.

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METHOD FOR MANUFACTURING A FABRIC REINFORCED COMPOSITE ARTICLE HAVING BALLISTIC RESISTANCE

The present invention relates to a method for manufacturing a fabric reinforced composite article having ballistic resistance and durability. The fabric reinforced composite articles manufactured by means of the present invention include a helmet, a tank protector, a bulletproof vest, a bulletproof panel and a bulletproof container.

According to one aspect of the invention, there is provided a method for manufacturing a fabric reinforced composite article having ballistic resistance wherein aliphatic polyamide filament yarn fabrics and aromatic polyamide filament yarn fabrics are respectively dipped into a solution of resin, dried, made into prepregs, cut into proper size, stacked with aliphatic polyamide prepregs as the outer layers and aromatic polyamide prepregs as the inner layers to the extent of a predetermined thickness, and heated and pressurized, wherein the aliphatic polyamide filament yarn fabrics are heat-treated, and then the aliphatic polyamide filament yarn fabrics and aromatic polyamide filament yarn fabrics are pre-heated prior to dipping into a solution of the resin.

According to another aspect of the invention, there is provided a method for manufacturing a fabric reinforced composite article having improved ballistic resistance, in which semihardened prepregs are made by dipping heat-treated and then pre-heated aliphatic polyamide filament yarn fabric and pre-heated aromatic polyamide filament yarn fabric respectively into a solution of phenolformaldehyde, or into a solution of epoxy resin, or into a solution of vinylester, or into a solution of resin composed of unsaturated polyester, such solutions also including polyvinyl butyral and methanol, and these prepregs are cut into proper size and stacked, heated and pressurized.

The prior methods employed to provide a helmet with bullet-proof properties and durability include one method in which prepregs obtained by dipping aliphatic polyamide filament yarn fabric into a solution of resin composed of phenol resin and methanol are heated and pressurized after being stacked, and another method in which aliphatic polyamide filament yarn fabric and aromatic polyamide filament yarn fabric dried after being dipped respectively into a solution of phenol resin,

or into a solution of epoxy resin, are cut into proper size and stacked exclusively or alternately, heated and pressurized.

However, manufacture of the composite article according to such prior methods as described above lowers not only the tensile strength and ballistic resistance because fabrics dipped into a solution of resin are exfloriated by virtue of lower adhesive strength between resin and fabric, but also production efficiency due to the contraction of fabrics dipped into a solution of resin when heated and pressurized. Moreover, the product has a shortened life by reason of surface rupture and presents a flexing fatigue problem and a stacking layer separation problem.

In order to overcome or mitigate such problems, the present invention provides that the aliphatic polyamide filament yarn fabric is heat-treated and then aliphatic polyamide yarn fabric and the aromatic polyamide filament yarn fabric are pre-heated respectively prior to dipping into a solution of the resin.

Preferred methods according to the invention will now be described in more detail.

After aliphatic polyamide filament yarn(250 - 1,500 denier) is woven into fabric(warp and weft desity is 30 - 100 threads/inch) and heat-treated at 100 - 200 °C for 1 - 10 minutes and after aromatic polyamide filament yarn(1,000 - 3,000 denier) is woven into fabric(warp and weft density is 30 - 100 threads/inch), these fabrics are pre-heated at 50 - 150 °C for 1 - 10 minutes,

and dipped into a solution of phenolformaldehyde, or into a solution of epoxy resin, or into a solution of vinylester, or into a solution of thermosetting resin composed of unsaturated polyester, these solutions also containing polyvinyl butyral and methanol. After drying at 50 - 150 °C for 1 - 10 minutes, they are made into semihardened prepregs and cut into proper size. In the case of the aliphatic polyamide filament yarn, it is generally found that the heat treatment and the pre-heating are both necessary, the temperature of the former normally being higher than that of the latter. Then, the prepregs are stacked so as to have 5 - 18 aliphatic polyamide prepregs as the outer layer and 1 - 10 aromatic polyamide prepregs as the inner layer. Thereafter, the stacked prepregs are heated at 50 - 120 °C and pressurized at 50 - 300 Kg/cm^2 and then cooled.

If a high pre-heating temperature is used some limited quenching or cooling may be desirable before dipping bearing in mind e.g. the boiling point of methanol.

A preferred solution of thermosetting resin for use in the present invention, is desirably composed of 5 - 30 wt% of polyvinyl butyral, 5 - 40 wt% of methanol and 10 - 90 wt% of phenolformaldehyde, or epoxy resin, or vinylester or unsaturated polyester. It is also desirable that the resin content(RC) and the volatile content(VC) of aliphatic polyamide filament yarn fabric and aromatic polyamide filament yarn fabric amount to 5 - 40 wt% and 1 - 10 wt% respectively. The VC as referred to above means the amount of solvent which escapes in vapor form when a fabric is dried after being dipped into the resin solution.

The reason that the aliphatic polyamide filament yarn fabric is heat-treated in the present invention is to increase its thermal stability and strength by reducing the remaining contractibility of the aliphatic polyamide filament yarn and increasing its degree of molecular orientation, and to promote an affinity between the resin and the fabric by lowering the amount of emulsion contained in the fabric.

Also, the reason that an aliphatic polyamide filament yarn fabric and an aromatic polyamide filament yarn fabric are preheated is to shorten the bonding time and the curing time of the fabric in view of the fact that resin is quickly bonded with the fabric at a high temperature.

The reason that aliphatic polyamide prepregs are used the outer layers and aromatic polyamide prepregs are used as the inner layers is to maximize ballistic resistance by arranging for highly stretchable aliphatic polyamide prepregs to arrest the initial impact and highly elastic aromatic polyamide prepregs to resist the remaining impact(penetration power).

The reason that polyvinyl butyral is added to a solution of resin when prepregs are manufactured in the present invention is to make the external appearance of the prepregs attractive and to strengthen the bonding power between fabric and resin to a considerable degree.

Although aliphatic or aromatic polyamide filament yarn can be woven into fabric by plain weave, twill weave, basket weave or satin weave, plain weave is most desirable for the present invention.

Helmets, bulletproof vests and bulletproof containers which are fabric reinforced composite articles manufactured by means of the present invention, have proved to be excellent not only in ballistic resistance and impact resistance but also in external appearance and durability.

Example 1

(1) Basket fabric(density 36 x 36 threads/inch) was woven of aliphatic polyamide filament yarn(840 denier, tensile strength 7 g/d, elongation 20 %).
It was relaxed at 100 °C for 5 minutes and then heat-treated at 150 °C for 1 minute.

(2) Plain fabric(density 17 x 17 threads/inch) was woven of aromatic polyamide filament yarn(3,000 denier, tensile strength 20 g/d, elongation 3 %).

The above fabrics(1)(2) were respectively pre-heated at 90 °C for 5 minutes. dipped into a solution of resin composed of 50 wt% of phenolformaldehyde(or epoxy resin, or vinylester, or unsaturated polyester), 10 wt% of polyvinyl butyral and 40 wt% of methanol. They were removed and found to have 36 wt% or 16 wt% resin content and 2 wt% in volatile content, and then dried at 120 °C for 5 minutes.

Then, they were made into prepregs and cut into the required size. Next, 12 sheets of aliphatic polyamide prepregs were stacked as the outer layers and 3 sheets of aromatic polyamide prepregs were stacked as the inner layers, 1 sheet of aliphatic

polyamide prepreg(RC 36 wt%) + 11 sheets of aliphatic polyamide prepregs(RC 16 wt%) + 2 sheets of aromatic polyamide prepregs (RC 16 wt%) + 1 sheet of aromatic polyamide prepreg(RC 36 wt%) being stacked in the indicated order working from the outermost layer. After they were molded by being heated and pressurized at 160 °C and 100 Kg/cm^2, they were cooled in 20 °C water for 10 minutes and made into a bulletproof helmet. Results of a test on the helmet are shown in Table 1.

Example 2

(1) 1/2 Basket weave fabric(density 36 x 36 threads/inch) was woven of aliphatic polyamide filament yarn(840 denier, tensile strangth 7 g/d, elongation 20 %) and relaxed at 100 ° C for 5 minutes.

(2) Plain weave fabric(density 17 x 17 threads/inch) was woven of aromatic polyamide filament yarn(3,000 denier, tensile strength 20 g/d, elongation 3 %).

The above fabrics(1)(2) were made into a bulletproof helmet in the same manner as described in Example 1 but without the pre-heating process. Results of a test on the helmet are as shown in Table 1.

Example 3

The two fabrics were made up in the same manner as described in Example 1, but a bulletproof helmet was made by using aromatic polyamide prepregs as the outer layers and aliphatic polyamide prepregs as the inner layers. Results of a test on the helmet are as shown in Table 1.

Table 1

Test \ Example		Example 1	Example 2	Example 3
Ballistic resistance(V_{50}) (feet/sec)		1,650	1,650	1,400
Flexing fatigue resistance		Stacked layers were not separated and surface was not cracked	Stacked layers separated and surface was cracked	Stacked layers were not separated and surface was not cracked
Impact resistance		Good	Good	Good
Heating and pressurizing test		Resin was not exfoliated nor transformed	Resin was exfoliated and transformed	Resin was not exfoliated nor transformed
Impregnating time and Curing time (min.)	Aliphatic polyamide fabric	2	4	2
	Aromatic polyamide fabric	3	6	3

(1) Ballistic resistance test : MIL - STD - 662 E, Caliber 0.22
Fragment weight 17 grain

(2) Flexing fatigue resistance : UK MOD SC 4796 A

(3) Impact resistance : A steel ball(3.6 $\pm$ 0.3 Kg, diameter 10 cm) was dropped from the height of 1.5 m

(4) Heating and pressurizing test :
Put in a heating and pressurizing pot saturated at 1.2 $\pm$ 0.1 Kg/cm^2
for 90 minutes at 90 °C

(5) The impregnating time of resin with a fabric and its curing time was measured when the fabric passed through a curing chamber at 25 m/min

CLAIMS

1. A method for manufacturing a fabric reinforced composite article having ballistic resistance wherein aliphatic polyamide filament yarn fabrics and aromatic polyamide filament yarn fabrics are respectively dipped into a solution of resin, dried, made into prepregs, cut into proper size, stacked with aliphatic polyamide prepregs as the outer layers and aromatic polyamide prepregs as the inner layers to the extent of a predetermined thickness, and heated and pressurized, wherein the aliphatic polyamide filament yarn fabrics are heat-treated, and then the aliphatic polyamide filament yarn fabrics and aromatic polyamide filament yarn fabrics are pre-heated prior to dipping into a solution of the resin.

2. A method according to claim 1, wherein aliphatic polyamide filament yarn fabric is heat-treated at 100 - 200 ^{o}C for 1 - 10 minutes and then pre-heated at 50 - 130 ^{o}C for 1 - 10 minutes.

3. A method according to claim 1 or 2, wherein the aromatic polyamide filament yarn fabric is pre-heated at 50 - 150 ^{o}C for 1 - 10 minutes.

4. A method according to any preceding claim, wherein the aliphatic polyamide filament yarn fabric is of 250 - 1,500 denier and of 30 - 100 threads/inch in warp and weft density.

5. A method according to any preceding claim, wherein the aromatic polyamide filament yarn fabric is of 1,000 - 3,000 denier and of 30 - 100 threads/inch in warp and weft density.

6. A method according to any preceding claim, wherein the resin solution comprises phenolformaldehyde or epoxy resin or vinylester or unsaturated polyester; polyvinyl butyral; and methanol.

7. A method according to any preceding claim, wherein the stacked prepregs are heated and pressurized at 50 - 200 ^{0}C and at 50 -300 Kg/cm^2 for 1 - 30 minutes.

8. A method according to claim 1 substantially as described in Example 1.

9. A fabric-reinforced composite article, when made by a method according to any preceding claim.

10. An article according to claim 9, which is a bulletproof helmet.

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